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Abstract

Near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$, formed from visible light ($\lambda > 420 \text{ nm}$) irradiation of $\text{Ru}_3(\text{CO})_{12}$, in alkane solution containing excess 1,4-pentadiene at 298 K yields $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ even in the presence of $\sim 1 \text{ M}$ 1,4-pentadiene. The complex $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ isomerizes to the thermodynamically more stable conjugated diene complex, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ with a half-time of about 2 minutes at 298 K. Near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ in rigid methylcyclohexane glasses containing $\sim 1 \text{ M}$ 1,4-pentadiene at 77 K yields $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ as the major product ($\sim 75\%$), but $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_7)$ is also observed as a minor product ($\sim 25\%$) which isomerizes to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ above 198 K. Room temperature photolysis of $\text{Ru}(\text{CO})_4(\eta^2\text{-3-methyl-1,4-pentadiene})$ in the presence of 3-methyl-1,4-pentadiene gives $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ and this species reacts to give a 1,3-diene complex with a half-time of $> 3 \text{ h}$. Near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,5-hexadiene})$ in the presence of $\sim 1 \text{ M}$ 1,5-hexadiene yields the non-conjugated diene complex, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$. In contrast to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$ is stable for hours in alkane solution at 298 K. Near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,6-heptadiene})$ in the presence of $\sim 1 \text{ M}$ 1,6-heptadiene does not generate a chelating diene complex $\text{Ru}(\text{CO})_3(\eta^4\text{-1,6-heptadiene})$ but rather the bis-olefin

complex $\text{Ru}(\text{CO})_3(\eta^2\text{-1,6-heptadiene})_2$. Thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with $\sim 1 \text{ M}$ diene = 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene and 1,6-heptadiene yields the same products as observed from photolysis of $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$ in $\sim 1 \text{ M}$ diene at 298 K.



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Technical Report #23

Thermal Reactions of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with Acyclic, Non-
conjugated Dienes and Photochemistry of $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$
Complexes

by

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Thermal Reactions of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with Acyclic, Non-
conjugated Dienes and Photochemistry of $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$
Complexes

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Abstract

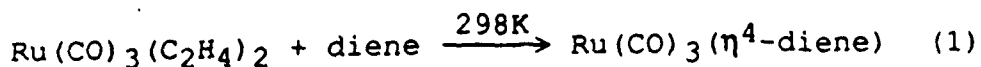
Near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$, formed from visible light ($\lambda > 420 \text{ nm}$) irradiation of $\text{Ru}_3(\text{CO})_{12}$, in alkane solution containing excess 1,4-pentadiene at 298 K yields $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ even in the presence of $\sim 1 \text{ M}$ 1,4-pentadiene. The complex $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ isomerizes to the thermodynamically more stable conjugated diene complex, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ with a half-time of about 2 minutes at 298 K. Near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ in rigid methylcyclohexane glasses containing $\sim 1 \text{ M}$ 1,4-pentadiene at 77 K yields $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ as the major product ($\sim 75\%$), but $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_7)$ is also observed as a minor product ($\sim 25\%$) which isomerizes to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ above 198 K. Room temperature photolysis of $\text{Ru}(\text{CO})_4(\eta^2\text{-3-methyl-1,4-pentadiene})$ in the presence of 3-methyl-1,4-pentadiene gives $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ and this species reacts to give a 1,3-diene complex with a half-time of $> 3 \text{ h}$. Near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,5-hexadiene})$ in the presence of $\sim 1 \text{ M}$ 1,5-hexadiene yields the non-conjugated diene complex, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$. In contrast to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$ is stable for hours in alkane solution at 298 K. Near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,6-heptadiene})$ in the presence of $\sim 1 \text{ M}$ 1,6-heptadiene does not generate a chelating diene complex $\text{Ru}(\text{CO})_3(\eta^4\text{-1,6-heptadiene})$ but rather the bis-olefin

complex $\text{Ru}(\text{CO})_3(\eta^2\text{-1,6-heptadiene})_2$. Thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with $\sim 1 \text{ M}$ diene = 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene and 1,6-heptadiene yields the same products as observed from photolysis of $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$ in $\sim 1 \text{ M}$ diene at 298 K.

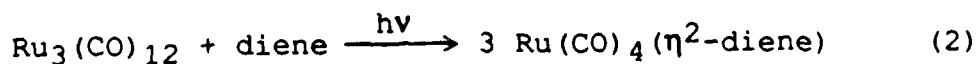
We wish to report the photochemistry of $\text{Ru}(\text{CO})_4(\eta^2\text{diene})$ (diene = 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene) complexes and the thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with these dienes. We¹⁻⁴ and others⁵⁻⁹ have previously reported the photochemical generation of catalytic intermediates at low temperatures as a means of investigating reactions of alkene complexes. In particular, we examined the photoassisted alkene isomerization catalysts derived from $\text{Fe}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$.¹⁰⁻¹³ The key intermediate, $\text{HM}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$, can be observed spectroscopically in a low temperature matrix.¹⁴ However, the absence of synthetic routes to $\text{M}(\text{CO})_n(\text{non-conjugated diene})$ complexes has hindered mechanistic studies of transition metal carbonyl catalyzed isomerization of non-conjugated dienes. → pentadienes.
(n-pen)
↑ An attempted synthesis that we tried, near-UV irradiation of an alkane solution of $\text{Ru}_3(\text{CO})_{12}$ and 1,4-pentadiene, yields $\text{Ru}(\text{CO})_3(1,3\text{-pentadiene})$ without build-up of the intermediate(s). $\text{Ru}(\text{CO})_3(1,5\text{-cyclooctadiene})$ undergoes reaction with 1,4-pentadiene at 100 °C to give directly $\text{Ru}(\text{CO})_3(1,3\text{-pentadiene})$.¹⁴ Thus, both pathways to form pentadiene complexes yield isomerization of the 1,4-diene to give a conjugated diene complex.

Here, we report the use of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ ¹ as a "Ru(CO)₃" transfer reagent permitting preparation of the new, thermally labile complexes, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$, $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ and

$\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$, equation (1). The η^4 -diene



complexes are reactive. For example, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ isomerizes rapidly at 298 K to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ probably via $\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})$. The complexes $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$, $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$, and $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$ can also be obtained by near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$ in alkane solution at 298 K. The $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$ complexes can be cleanly made with excess diene via visible light ($\lambda > 420 \text{ nm}$) photolysis of $\text{Ru}_3(\text{CO})_{12}$ where $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$ does not absorb, equation (2).



Experimental

Materials. All solvents were reagent grade and freshly distilled before use. The $\text{Ru}_3(\text{CO})_{12}$ was obtained from Strem Chemicals and was used as received. The photochemistry at low temperature was carried out using methylcyclohexane (J.T. Baker) as the matrix material. The 1,3-pentadiene, 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, and 1,6-heptadiene were obtained from Aldrich and passed through Al_2O_3 prior to use. Research grade C_2H_4 was obtained from Matheson. The PPh_3 was recrystallized prior to use.

Instrumentation. IR spectra were recorded using a Nicolet 7199 or 60SX Fourier transform IR spectrometer. UV-VIS spectra were recorded using a Hewlett Packard 8451A Diode Array spectrometer. Gas chromatograph-mass spectra (GC-MS) were recorded on a Hewlett-Packard model 5992 mass spectrometer. All mass spectra were recorded at 70 ev. Separations were done using a 10 ft. x 1/8 in. SE-30 on chromasorb W column. A Model A High Energy Micro Pulser from Xenon Cooperation was used for flash photolysis. The pulser is equipped with the Xenon FP series of Micropulse Flashtubes used at a discharge voltage of ~5 kilovolts.

Procedures. Generally, all manipulations were carried out under N_2 in a Vacuum Atmospheres dry box or under Ar using conventional Schlenk line techniques. Low temperature irradiations involved the use of a Bausch and Lomb SP200 200 W high pressure Hg lamp filtered with a 10 cm Pyrex water filter. Low temperature IR spectra were recorded using a

Precision Cell, Inc. Model P/N 21.000 variable temperature cell equipped with CaF_2 windows.

Solutions of $\sim 1 \text{ mM}$ $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ were prepared according to the literature procedure,¹ and all solutions of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ were saturated with C_2H_4 to prevent decomposition. In a typical procedure, the $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ was prepared quantitatively via visible light ($\lambda > 420 \text{ nm}$) irradiation of 0.4 mM $\text{Ru}_3(\text{CO})_{12}$ in a continuously C_2H_4 -purged alkane solution using a filtered Hanovia 550 W medium pressure Hg lamp. The $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ solution were prepared by subsequent near-UV irradiation of a $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ solution at 298 K in the presence of C_2H_4 . Only $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ and $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ were spectroscopically detected in these solutions. After $\sim 90\%$ conversion of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$, the photolysis was stopped and the solution was purged with C_2H_4 to remove photogenerated CO . All thermal reactions with dienes according to equation (1) were carried out using freshly prepared solutions of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. IR data for complexes studied are found in Table I. In general we are not able to isolate the $\text{Ru}(\text{CO})_n(\text{olefin})_{5-n}$ ($n = 4, 3$) complexes or obtain clean NMR data, since these complexes are stable only in the presence of excess olefin.

$\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$, $\text{Ru}(\text{CO})_4(\eta^2\text{-3-methyl-1,4-pentadiene})$, $\text{Ru}(\text{CO})_4(\eta^2\text{-1,5-hexadiene})$, and $\text{Ru}(\text{CO})_4(\eta^2\text{-1,6-heptadiene})$ were prepared via a modification of the preparation for $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$. Visible light ($\lambda > 420 \text{ nm}$)

irradiation of $\sim 0.4 \text{ mM}$ $\text{Ru}_3(\text{CO})_{12}$ in a 3-methylpentane solution containing $\sim 1 \text{ M}$ diene at 298 K cleanly yields $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$.

Results and Discussion

(a) **Thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 1,4-Pentadiene and 3-methyl-1,4-pentadiene.** Addition of 1,4-pentadiene to a concentration of $\sim 1 \text{ M}$ to an alkane/ C_2H_4 solution of $\sim 1 \text{ mM}$ $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, at 298 K leads to rapid IR spectral changes which are consistent with the substitution reaction represented by equation (3). The difference IR spectra in

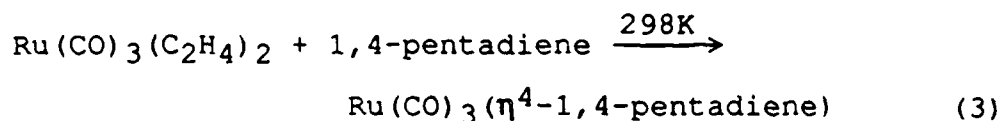
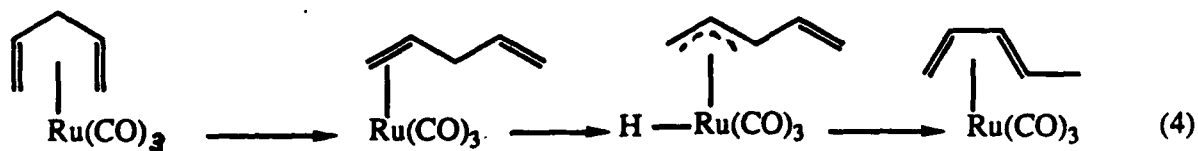


Figure 1 show that the three absorption bands in the CO stretching region due to $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ decrease in intensity immediately upon mixing, and two new bands at 2050, and 1966 cm^{-1} increase in intensity. The 2050, 1966 cm^{-1} bands in the IR spectrum differ from those observed for $\text{Ru}(\text{CO})_3(\text{alkene})_2$, $\text{Ru}(\text{CO})_3(\eta^4\text{-}1,3\text{-diene})$, and $\text{HRu}(\text{CO})_3(\eta^3\text{-allyl})$, Table I. We assign the bands at 2050 and 1966 cm^{-1} to the complex, $\text{Ru}(\text{CO})_3(\eta^4\text{-}1,4\text{-pentadiene})$. The $\text{Ru}(\text{CO})_3(\eta^4\text{-}1,4\text{-pentadiene})$ complex has a third CO stretching band at 1992 cm^{-1} , which is obscured in the difference IR spectra by the band at 1995 cm^{-1} due to $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$.

As reported earlier,¹ $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ reacts rapidly with L (L = CO, PPh_3 , alkene) yielding $\text{Ru}(\text{CO})_3(\text{L})_2$. However, there are no bands attributable to $\text{Ru}(\text{CO})_3(\eta^2\text{-}1,4\text{-pentadiene})_2$ in the IR spectrum from the reaction of

$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and $\sim 1 \text{ M}$ 1,4-pentadiene. We attribute the lack of formation of $\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})_2$ to the ability of 1,4-pentadiene to bind preferentially as a chelating ligand. Despite the thermodynamic chelate effect, the diene ligand in an alkane solutions of $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ is very rapidly replaced by reaction with 0.05 M PPh_3 yielding $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ within 1 min.

As shown in Figure 1, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ isomerizes with a half-time of about 2 min at 298 K to give $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ having bands at 2063, 1998, and 1987 cm^{-1} . The structure of this complex is assigned by comparison of IR and GC-mass spectral data with that from an authentic sample prepared independently by reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and 1,3-pentadiene. We presume¹⁵ that the isomerization of the 1,4-pentadiene occurs via dechelation of the diene, oxidative addition of an allylic C-H bond yielding a π -allyl hydride complex followed by reductive elimination of a new allylic C-H bond, equation (4).



Light-induced loss of CO from $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ can also yield the presumed coordinatively unsaturated $\eta^2\text{-}$

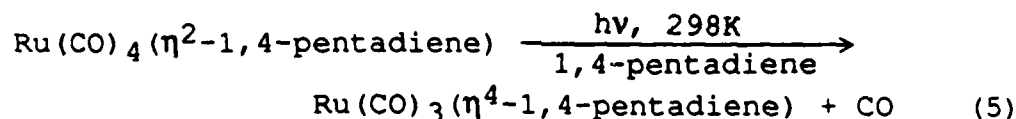
1,4-pentadiene intermediate and ultimately does yield the conjugated diene product (vide infra). Furthermore, low temperature photochemical experiments with $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$, vide infra, have been used to detect the π -allyl hydride intermediate.

Similar to 1,4-pentadiene, addition of $\sim 1 \text{ M}$ 3-methyl-1,4-pentadiene to an alkane/ C_2H_4 solution of $\sim 1 \text{ mM}$ $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ at 298 K also results in the rapid decline of IR spectral features for $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and growth of new features attributed to $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$, Figure 2a. The three CO stretching bands at 2052, 1994, and 1968 cm^{-1} for $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ are remarkable similar to those for $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$, Table I. $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ isomerizes with a half-time of $>3 \text{ h}$ at 298 K to $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,3-pentadiene})$, Figure 2b. The slow isomerization of $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ compared to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ is probably not only due to the replacement of one doubly-allylic hydrogen by a methyl group but is also due to steric hindrance associated with the methyl substituent in formation of a π -allyl hydride intermediate.

(b) Photoreaction of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ and $\text{Ru}(\text{CO})_4(\eta^2\text{-3-methyl-1,4-pentadiene})$ at 298 K. The complex $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ can be made via visible ($\lambda > 420 \text{ nm}$) irradiation of an alkane solution of $\text{Ru}_3(\text{CO})_{12}$ at 298 K, equation (2). The complex $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ is, however, only stable in the presence of an excess of 1,4-

pentadiene (1 M is typically used). The selective irradiation of $\text{Ru}_3(\text{CO})_{12}$ is a general and efficient way to synthesize $\text{Ru}(\text{CO})_4(\eta^2\text{-olefin})$ (olefin = C_2H_4 , C_3H_6 , C_5H_{10} , 1,3-pentadiene, 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene), Table I. Owing to thermodynamic considerations, it is logical to conclude that all of the η^2 -diene complexes involve the terminal double bond,¹⁶ but this has not been unambiguously established.

Xenon flash ($\sim 50 \mu\text{s}$) photolysis of $\sim 1 \text{ mM}$ $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ in a 3-methylpentane solution at 298 K containing $\sim 1 \text{ M}$ 1,4-pentadiene yields $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ via light-induced loss of CO, equation (5), Figure 3a. The difference IR spectrum of $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-}$



pentadiene) associated with this reaction shows the same bands for product as observed in the thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 1,4-pentadiene, Figure 1, except that the peak at 1992 cm^{-1} for $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ is less obscured by the peak at 1994 cm^{-1} of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$. The complex $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ isomerizes to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ as discussed above with a half-time of $\sim 2 \text{ min}$ at 298 K. Figure 3b shows IR spectral data for the isomerization reaction. The data reveal that both the $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ and

$\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ complexes clearly have three CO absorption bands.

Xenon flash photolysis of $\sim 1 \text{ mM}$ $\text{Ru}(\text{CO})_4(\eta^2\text{-3-methyl-1,4-pentadiene})$ in a 3-methylpentane solution at 298 K containing $\sim 1 \text{ M}$ 3-methyl-1,4-pentadiene yields $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ which shows the same bands as observed in thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 3-methyl-1,4-pentadiene. The follow-up thermal isomerization of $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ occurs with a half-time of $>3 \text{ h}$, as found from studies beginning with $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$.

(c) Photoreaction of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ in a methylcyclohexane glass. In order to observe the unstable intermediates associated with the chemistry in equations (4) and (5), we studied the photochemistry of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ in a methylcyclohexane matrix at 77 K. When $\sim 1 \text{ mM}$ $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ is irradiated in a rigid 1,4-pentadiene-containing ($\sim 1 \text{ M}$) glass, bands characteristic of free CO (2132 cm^{-1}) and $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ ($2048, 1960 \text{ cm}^{-1}$) are observed in the IR spectra, Figure 4. The rigid glass precludes diffusion of the presumed $\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})$ intermediate, thus ruling out polynuclear species as photoproducts. The rigid glass will, however, allow association of the free double bond of the $\eta^2\text{-1,4-pentadiene}$ ligand with the vacant coordination site resulting from loss of CO to give $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$. We have not observed any bands in the IR

spectra at 77 K assignable to $\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})$ which we presume to be the primary photoproduct. $\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})$ might be able to be observed at temperatures lower than 77 K, since $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$ has been observed upon photolysis of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ in a 3-methylpentane glass at 55 K,¹ Table I. Also, we do not find $\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})_2$ as a product which might be expected owing to the presence of excess 1,4-pentadiene. However, if the concentration of 1,4-pentadiene is increased from 1 M to 4 M, we do observe $\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})_2$ as a product (~20%) at 77 K. This assignment is based on IR spectral similarity to $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and other bis-olefin complexes, Table I.

There are important bands at 2080 and 2006 cm^{-1} in the IR spectra recorded after photolysis of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ at 77 K due to a second product (~25%), Figure 4. Based on the similarity of the frequencies and relative intensities of these bands to those for the known complexes $\text{HRu}(\text{CO})_3(\eta^3\text{-allyl})$ (allyl = C_3H_5 , C_5H_9), we assign the bands at 2080 and 2006 cm^{-1} to the allyl hydride complex $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_7)$, Table I. Evidently, association of the free olefin and oxidative addition of the allylic C-H bonds of the $\eta^2\text{-1,4-pentadiene}$ ligand in the presumed primary photoproduct, $\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})$, are competitive processes in the photolysis of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ at 77 K.

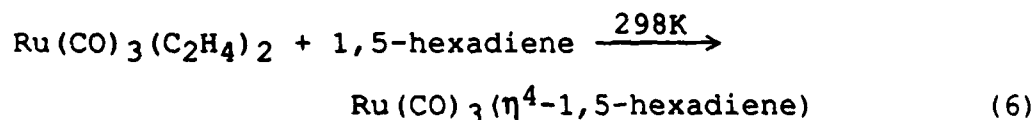
Warming the matrix containing the photogenerated

HRu(CO)₃(η³-C₅H₇) to 195 K results in the loss of the bands due to HRu(CO)₃(η³-C₅H₇) and growth in bands for Ru(CO)₃(η⁴-1,3-pentadiene). Bands due to photogenerated Ru(CO)₃(η⁴-1,4-pentadiene) survive the warmup process to 195 K. Further warmup to 298 K yields quantitative formation of Ru(CO)₃(η⁴-1,3-pentadiene). This experiment demonstrates that HRu(CO)₃(η³-C₅H₇) can be an intermediate in the photochemical formation of Ru(CO)₃(η⁴-1,3-pentadiene) from Ru(CO)₄(η²-1,4-pentadiene) and is chemically competent to be an intermediate in the thermal isomerization of Ru(CO)₃(η⁴-1,4-pentadiene) to Ru(CO)₃(η⁴-1,3-pentadiene).

The photochemistry of Ru(CO)₄(η²-1,4-pentadiene) in an alkane matrix at 77 K in the presence of excess 1,4-pentadiene and the thermal reaction of these intermediates when they are allowed to warm are summarized in Scheme I.

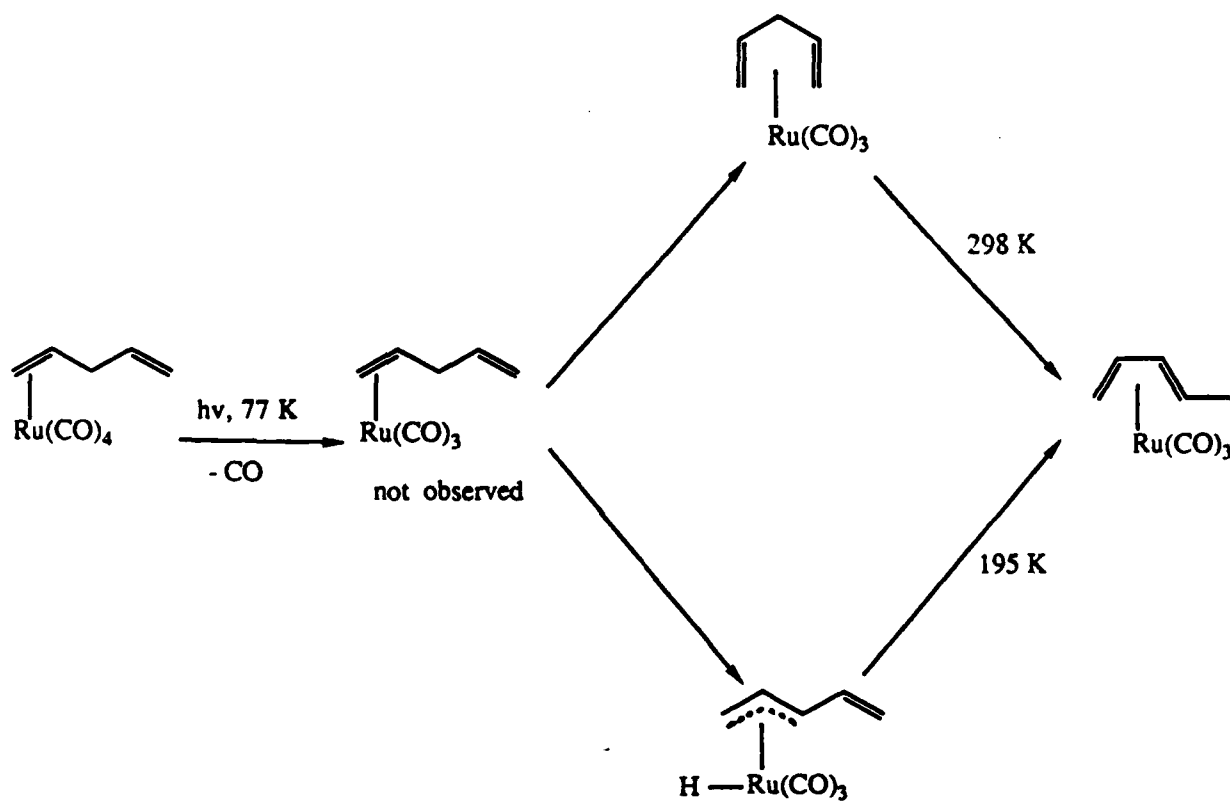
(d) Thermal reaction of Ru(CO)₃(C₂H₄)₂ with 1,5-hexadiene.

Addition of 1 M 1,5-hexadiene to an alkane solution of 1 mM Ru(CO)₃(C₂H₄)₂ at 298 K results in IR spectral changes consistent with the substitution reaction represented by equation (6). Two new bands at 2050 and 1966 cm⁻¹ appear in



the IR spectra and the bands due to Ru(CO)₃(C₂H₄)₂ decrease in intensity immediately after addition of 1,5-hexadiene to

Scheme I. Photochemistry of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$.



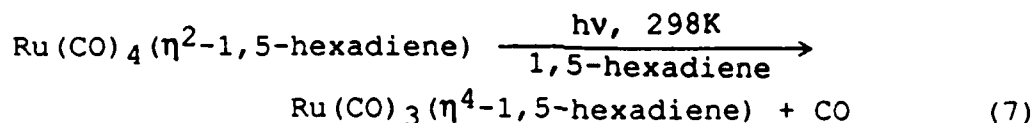
a solution of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, Figure 5. We assign the product in equation (6) to be $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$ based on its IR spectrum. The IR spectrum for the complex is remarkably similar to the IR spectra of $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ and $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$, Table I. The coordinated 1,5-hexadiene in $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$ can also be replaced within 1 min at 298 K by reaction with 0.05 M PPh_3 yielding $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$.

In contrast to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ or $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$, the complex $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$ is stable at 298 K in alkane solution under an inert atmosphere for hours. We attribute the rapid rate of isomerization of $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ to the presence of two doubly-allylic hydrogens in 1,4-pentadiene. Due to the steric effect of the methyl substituent on 3-methyl-1,4-pentadiene on the isomerization process $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$, with only one doubly-allylic hydrogen, shows a much slower rate of isomerization to $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,3-pentadiene})$. Despite the substitution lability of $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$, it is surprisingly inert to isomerization. However, $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ is not very active as an isomerization catalyst toward 1-pentene either, though the bis-1-pentene complex is very substitutionally labile.¹

(e) Photoreaction of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,5-hexadiene})$ at 298 K.

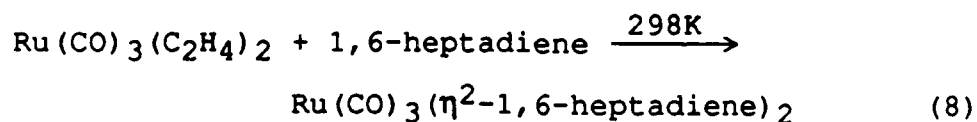
Flash photolysis of 1 mM $\text{Ru}(\text{CO})_4(\eta^2\text{-1,5-hexadiene})$ in a 3-

methylpentane solution at 298 K containing 1 M 1,5-hexadiene leads to IR spectral changes which are consistent with the reaction represented by equation (7). The difference IR spectrum in Figure 6 shows that the three bands for



$\text{Ru(CO)}_4(\eta^2\text{-1,5-hexadiene})$ decrease, and two new bands at 2050 and 1966 cm^{-1} increase in intensity. The positions of these bands are the same as those observed in the thermal reaction of $\text{Ru(CO)}_3(\text{C}_2\text{H}_4)_2$ with 1,5-hexadiene.

(f) Thermal reaction of $\text{Ru(CO)}_3(\text{C}_2\text{H}_4)_2$ with 1,6-heptadiene. Addition of ~1 M 1,6-heptadiene to an alkane solution of ~1 mM $\text{Ru(CO)}_3(\text{C}_2\text{H}_4)_2$ at 298 K results in IR spectral changes consistent with the substitution reaction represented by equation (8). The difference IR spectra in Figure 7 show

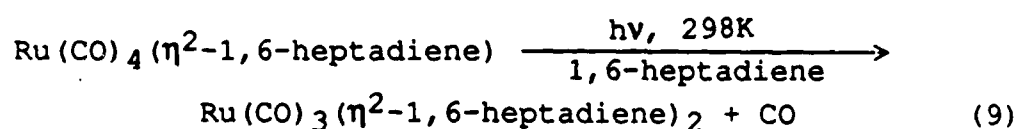


that the three CO absorption bands due to $\text{Ru(CO)}_3(\text{C}_2\text{H}_4)_2$ decrease in intensity immediately upon mixing, and new bands at 2074 and 1986 cm^{-1} attributed to $\text{Ru(CO)}_3(\eta^2\text{-1,6-heptadiene})_2$ increase in intensity. This assignment of the product is based on the spectral similarity to bis- C_2H_4 complex and other bis-olefin complexes. The shift to lower

frequencies is consistent with the substitution of C_2H_4 by 1,6-heptadiene, Table I. Interestingly, the product obtained from the reaction of $Ru(CO)_3(C_2H_4)_2$ and 1,6-heptadiene is not $Ru(CO)_3(\eta^4-1,6\text{-heptadiene})$ but $Ru(CO)_3(\eta^2-1,6\text{-heptadiene})_2$. The reactivity difference between 1,6-heptadiene and the 1,4- and 1,5-dienes with $Ru(CO)_3(C_2H_4)_2$ is presumably due to the fact that the two double bonds of 1,6-heptadiene are too far apart for a cooperative chelate effect. $Ru(CO)_3(\eta^2-1,6\text{-heptadiene})_2$ reacts with 0.05 M PPh_3 at 298 K yielding $Ru(CO)_3(PPh_3)_2$ within 1 min, demonstrating that it too is a very labile complex.

(g) Photochemistry of $Ru(CO)_4(\eta^2-1,6\text{-heptadiene})$ at 298 K.

Xenon flash photolysis of $Ru(CO)_4(\eta^2-1,6\text{-heptadiene})$ in an alkane solution containing 1 M 1,6-heptadiene results in the formation of $Ru(CO)_3(\eta^2-1,6\text{-heptadiene})_2$, equation (9).



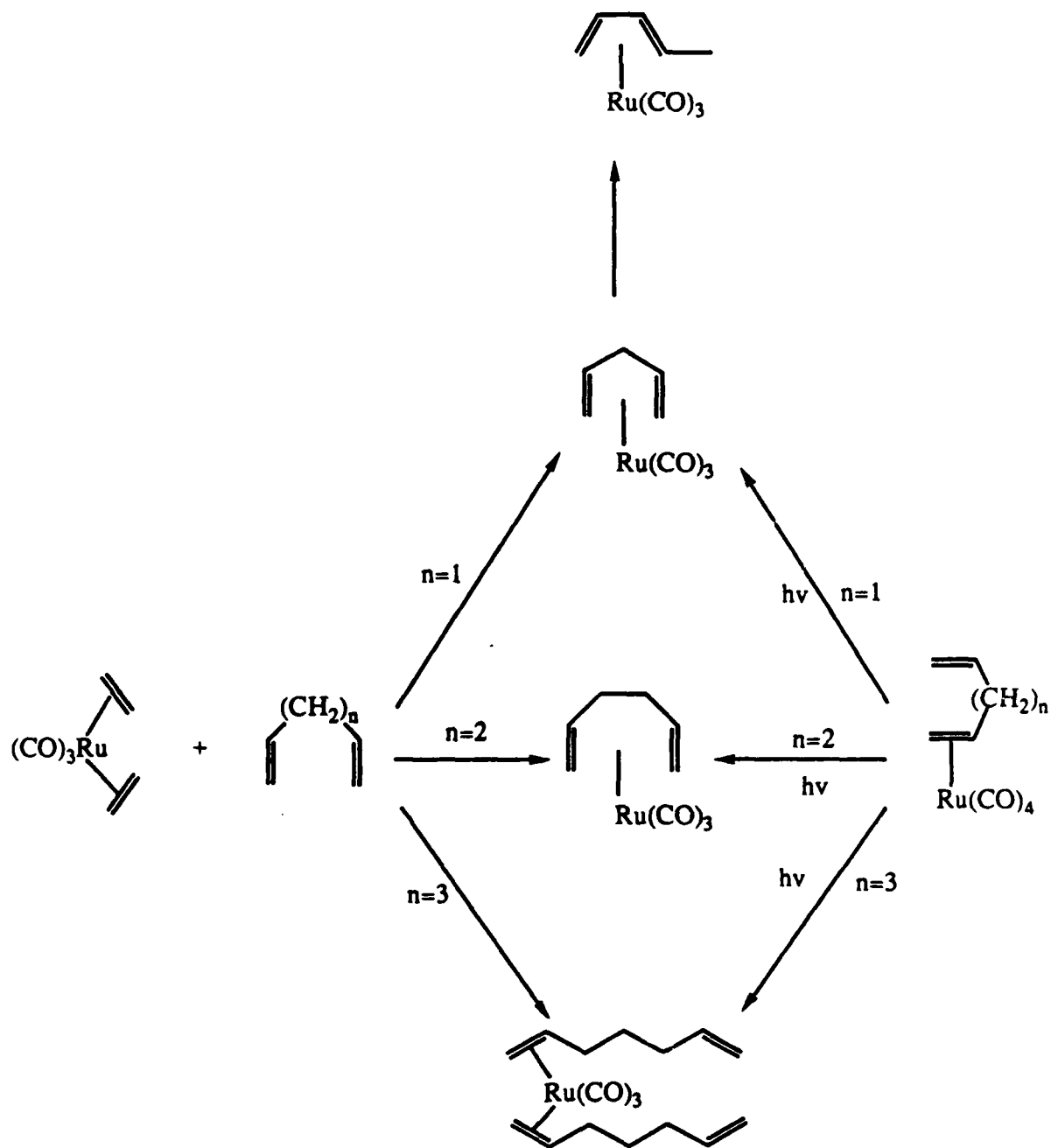
The IR spectrum of $Ru(CO)_3(\eta^2-1,6\text{-heptadiene})_2$ produced in this reaction shows the same bands as observed in the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,6-heptadiene.

Conclusions

As summarized in Scheme II, the photoreaction of $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$ and the thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with the diene give the same products. The products can be either $\text{Ru}(\text{CO})_3(\eta^4\text{-diene})$ or $\text{Ru}(\text{CO})_3(\eta^2\text{-diene})_2$, depending on the number of saturated carbons between terminal double bonds. The chelation effect is significant for 1,4-pentadiene, 3-methyl-1,4-pentadiene, and 1,5-hexadiene, but 1,6-heptadiene does not form a chelate complex.

The presence of two doubly-allylic hydrogens in $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ permits it to rapidly isomerize to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ at 298 K. Replacing one of the two doubly-allylic hydrogens by a methyl group significantly slows down the rate of isomerization at 298 K of $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ to $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,3-pentadiene})$. In contrast, $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$ is stable for several hours under the same conditions. We are not able to observe $\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})$ on irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ at 77 K. The significant products at 77 K are $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ and $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_7)$ which isomerizes to $\text{Ru}(\text{CO})_3(\eta^3\text{-1,4-pentadiene})$ above 195 K. Thus, low temperature photochemistry of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ provides evidence that $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_7)$ can be an intermediate in the isomerization of $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$.

Scheme II. Photochemistry of $\text{Ru}(\text{CO})_4(\eta^2\text{-diene})$ (diene = 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene) and thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and dienes in an alkane solution at 298 K.



We have demonstrated that $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ is not only a catalyst for alkene isomerization¹ but serves as a " $\text{Ru}(\text{CO})_3$ " transfer reagent, permitting the synthesis of novel, thermally labile ruthenium complexes of acyclic non-conjugated dienes.

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Table I. IR Data for Relevant Complexes

species	medium (T, K)	ν , cm^{-1} (rel abs)
$\text{Ru}_3(\text{CO})_{12}$	3MP ^a (298)	2061 (2.7), 2031 (1.6), 2012 (1.0)
$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$	3MP (298)	1907
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)^c$	3MP (55)	2055 (1.0), 1978 (1.2), 1972 (1.3)
$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$	3MP (298)	2104 (1.0), 2023 (17.2), 1996 (8.5)
$\text{Ru}(\text{CO})_4(\text{C}_3\text{H}_6)$	3MP (298)	2100 (1.0), 2018 (10.6), 1991 (6.4)
$\text{Ru}(\text{CO})_4(\text{C}_5\text{H}_{10})$	3MP (298)	2100 (1.0), 2018 (9.3), 1989 (5.8)
$\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$	3MP (298)	2101 (1.0), 2019 (9.5), 1994 (5.1)
	MCH ^b (298)	2101 (1.0), 2019 (10.7), 1993 (6.0)
	MCH (77)	2103 (1.0), 2020 (7.0), 1991 (5.4)
$\text{Ru}(\text{CO})_4(\eta^2\text{-3-methyl-C}_5\text{H}_7)^d$	3MP (298)	2101 (1.0), 2019 (9.1), 1993 (4.9)
$\text{Ru}(\text{CO})_4(\eta^2\text{-1,5-hexadiene})$	3MP (298)	2101 (1.0), 2019 (9.2), 1992 (5.0)
$\text{Ru}(\text{CO})_4(\eta^2\text{-1,6-heptadiene})$	3MP (298)	2100 (1.0), 2019 (9.6), 1992 (4.8)
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	3MP (298)	2081 (1.0), 2005 (7.1), 1995 (20.3)
$\text{Ru}(\text{CO})_3(\text{C}_3\text{H}_6)_2$	3MP (298)	2075 (1.0), 2005 (3.3), 1988 (14.0)
$\text{Ru}(\text{CO})_3(\text{C}_5\text{H}_{10})_2$	3MP (298)	2072 (1.0), 2005 (2.6), 1987 (9.4)
$\text{Ru}(\text{CO})_3(\eta^2\text{-1,4-pentadiene})_2$	MCH (77)	2077 (1.0), 2002 (3.0), 1994 (6.1)
$\text{Ru}(\text{CO})_3(\eta^2\text{-1,6-heptadiene})_2$	3MP (298)	2074 (1.0), 1998 (2.5), 1986 (9.8)
$\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$	3MP (298)	2050 (1.1), 1992 (1.0), 1966 (1.0)
	MCH (77)	2048 (1.0), 1992 (1.0), 1960 (1.1)
$\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-C}_5\text{H}_7)^d$	3MP (298)	2052 (1.2), 1994 (1.1), 1968 (1.0)
$\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$	3MP (298)	2050 (1.1), 1994 (1.1), 1966 (1.0)
$\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$	3MP (298)	2063 (1.0), 1998 (1.6), 1987 (1.4)
$\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,3-C}_5\text{H}_7)^e$	3MP (298)	2061 (1.0), 1996 (1.5), 1983 (1.4)
$\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-butadiene})^f$	Hexane (298)	2069 (s), 2006 (vs), 1995 (s)
$\text{HRu}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$	MCH (77)	2082 (1.0), 2008 (1.2)
$\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_9)$	MCH (77)	2078 (1.0), 2004 (1.2)
$\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_7)$	MCH (77)	2080 (1.0), 2006 (1.2)

^a 3MP = 3-methylpentane.

^b MCH = methylcyclohexane.

^c Band positions obtained from ref 1.

^d 3-methyl-1,4-C₅H₇ = 3-methyl-1,4-pentadiene.

^e 3-methyl-1,3-C₅H₇ = 3-methyl-1,3-pentadiene.

^f Band positions obtained from ref 14.

Figure Captions

Figure 1. IR difference spectral changes accompanying thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 1,4-pentadiene in 3-methylpentane solution at 298 K ($\Delta t = 60, 90, 120, 180$ s). The positive peaks at 2050 and 1966 cm^{-1} are due to the intermediate $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$. The spectra were taken as the concentration of this intermediate was decreasing with time and isomerizing to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$. The positive peaks at 2063, 1998, and 1987 cm^{-1} are due to this product.

Figure 2. (a) IR difference spectral changes accompanying thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 3-methyl-1,4-pentadiene in 3-methylpentane solution at 298 K ($\Delta t = 30, 60, 90$ s). The positive peaks at 2052 and 1968 cm^{-1} correspond to $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$. (b) IR difference spectral changes accompanying thermal isomerization of $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,4-pentadiene})$ from (a) in 3-methylpentane solution at 298 K ($\Delta t = 30, 60, 90$ min). The positive peaks at 2061, 1996, 1983 cm^{-1} correspond to $\text{Ru}(\text{CO})_3(\eta^4\text{-3-methyl-1,3-pentadiene})$.

Figure 3. (a) IR difference spectral changes measured ~ 1 min after a $50\text{ }\mu\text{s}$ flash photolysis of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ in 3-methylpentane solution containing $\sim 1\text{ M}$ 1,4-pentadiene at 298 K. The positive peaks at 2050, 1992, and 1966 cm^{-1} correspond to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$. (b) IR difference spectral changes accompanying thermal isomerization of $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$ from (a) in 3-

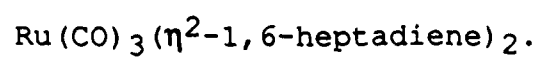
methylpentane solution at 298 K ($\Delta t = 30, 60, 120$ s). The positive peaks at 2063, 1998, and 1987 cm^{-1} correspond to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$.

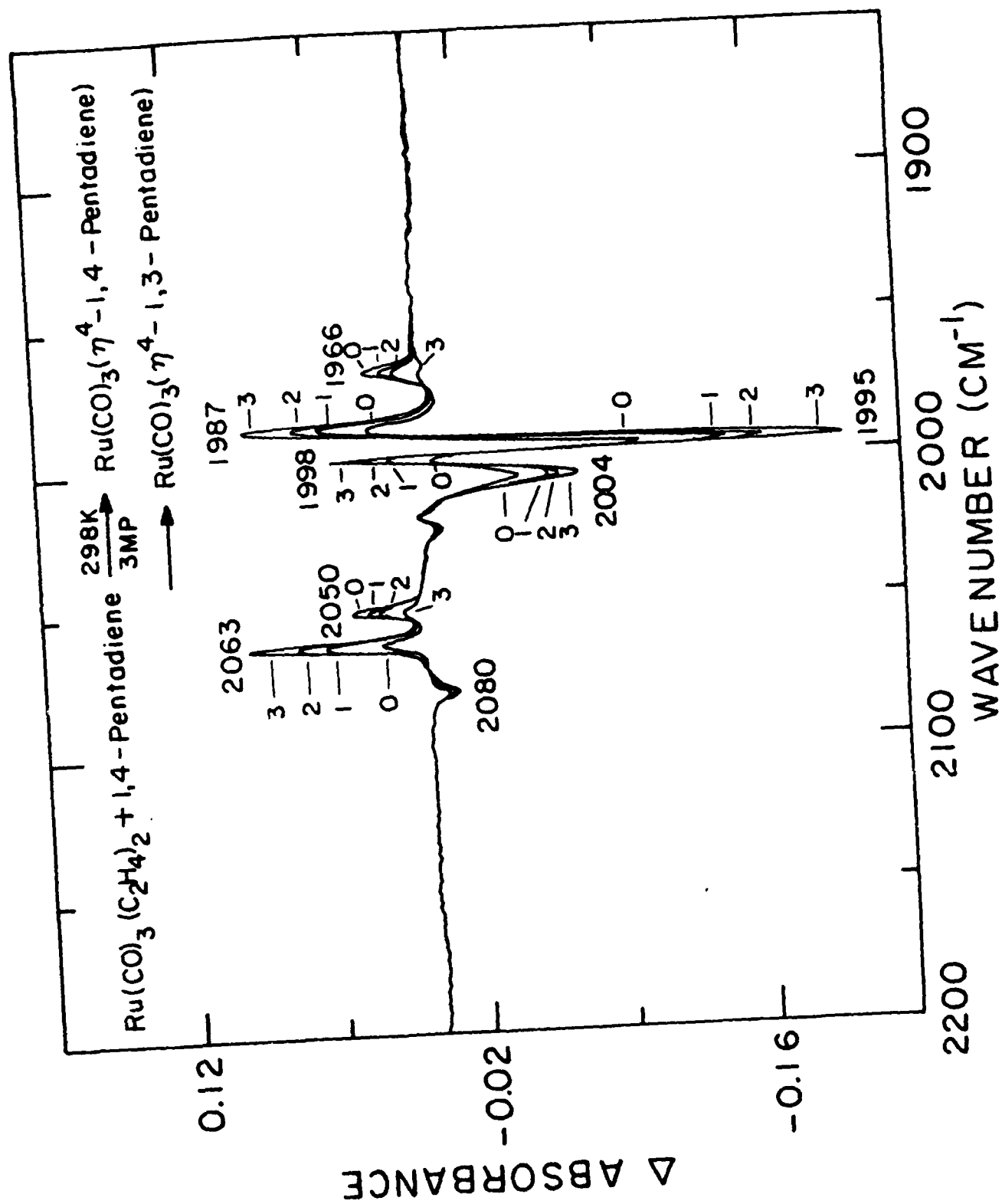
Figure 4. IR difference spectral changes due to near-UV irradiation of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,4-pentadiene})$ in a methylcyclohexane matrix containing $\sim 1\text{ M}$ 1,4-pentadiene at 77 K. The positive peaks at 2048 and 1960 cm^{-1} are due to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,4-pentadiene})$, the peaks at 2080 and 2006 cm^{-1} are due to $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_7)$, and the peak at 2132 cm^{-1} is due to free CO.

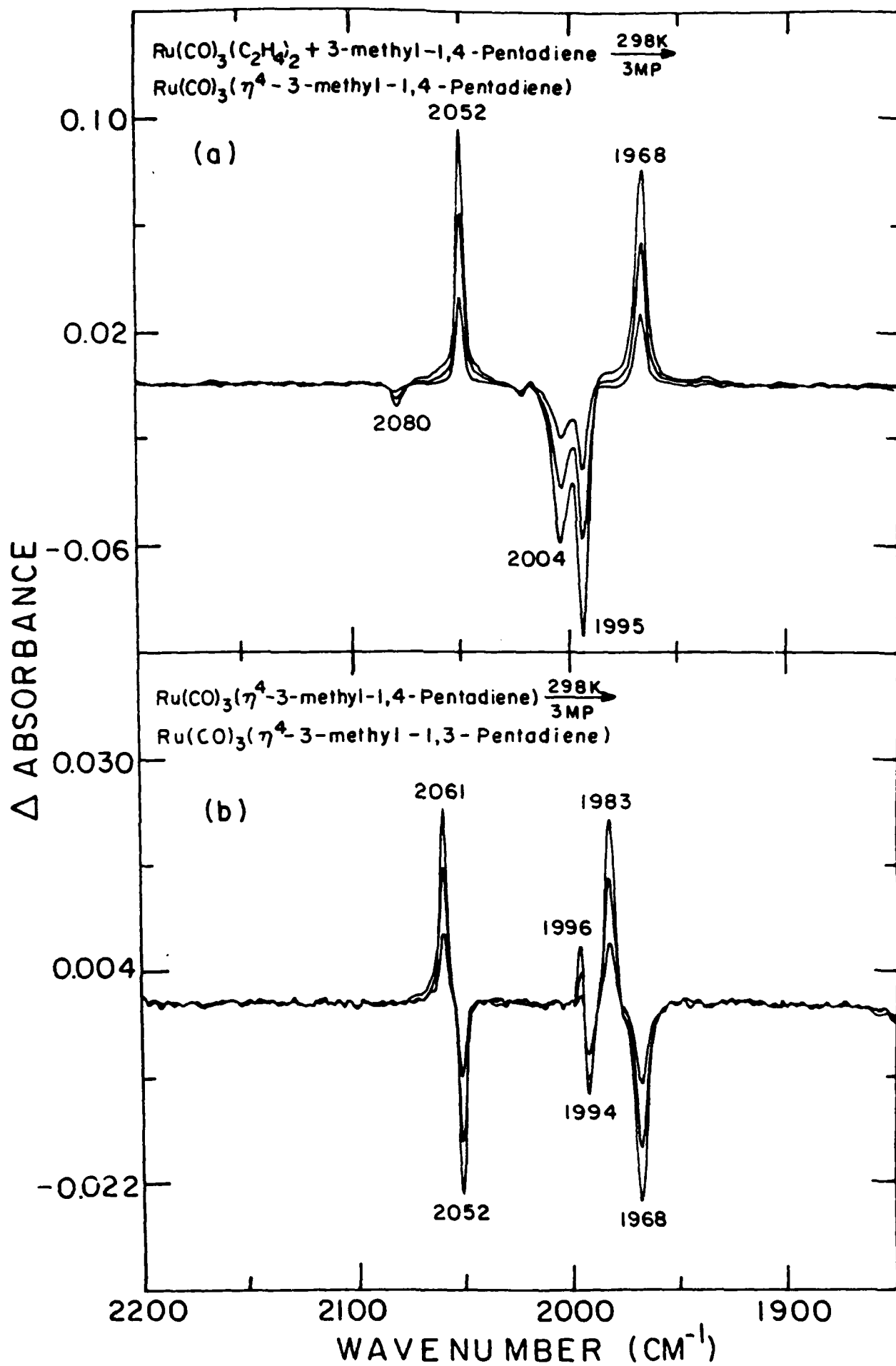
Figure 5. (a) IR difference spectral changes accompanying thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 1,5-hexadiene in 3-methylpentane solution at 298 K ($\Delta t = 30, 60, 90$ s). The positive peaks at 2050 and 1966 cm^{-1} correspond to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$. (b) IR spectrum for $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$ after thermal reaction from (a) completed. The peak at 2019 cm^{-1} is due to trace amount of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,5-hexadiene})$.

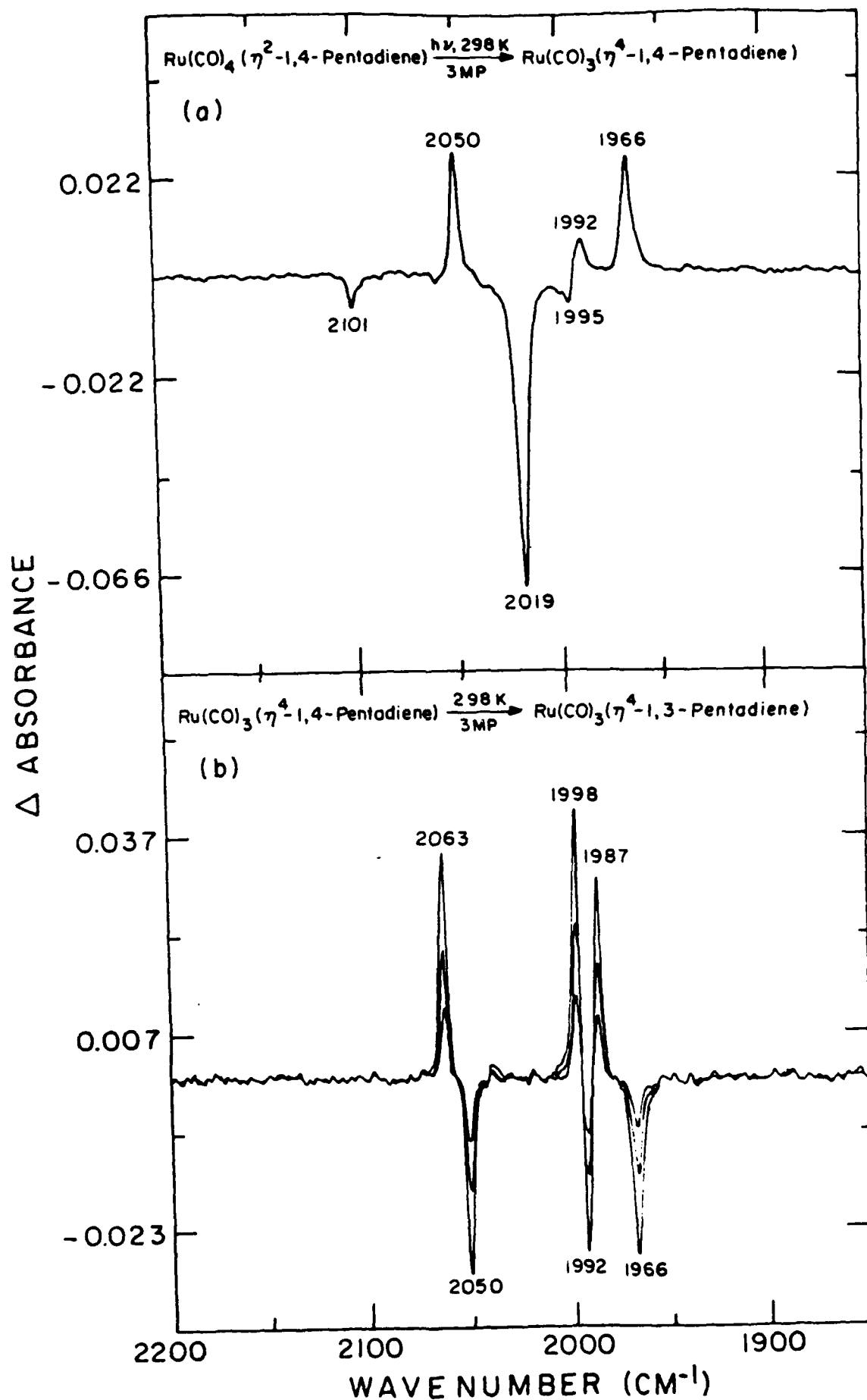
Figure 6. IR difference spectral changes measured ~ 1 min after a $50\text{ }\mu\text{s}$ flash photolysis of $\text{Ru}(\text{CO})_4(\eta^2\text{-1,5-hexadiene})$ in a 3-methylpentane solution containing $\sim 1\text{ M}$ 1,5-hexadiene at 298 K. The positive peaks at 2050 and 1966 cm^{-1} are due to $\text{Ru}(\text{CO})_3(\eta^4\text{-1,5-hexadiene})$.

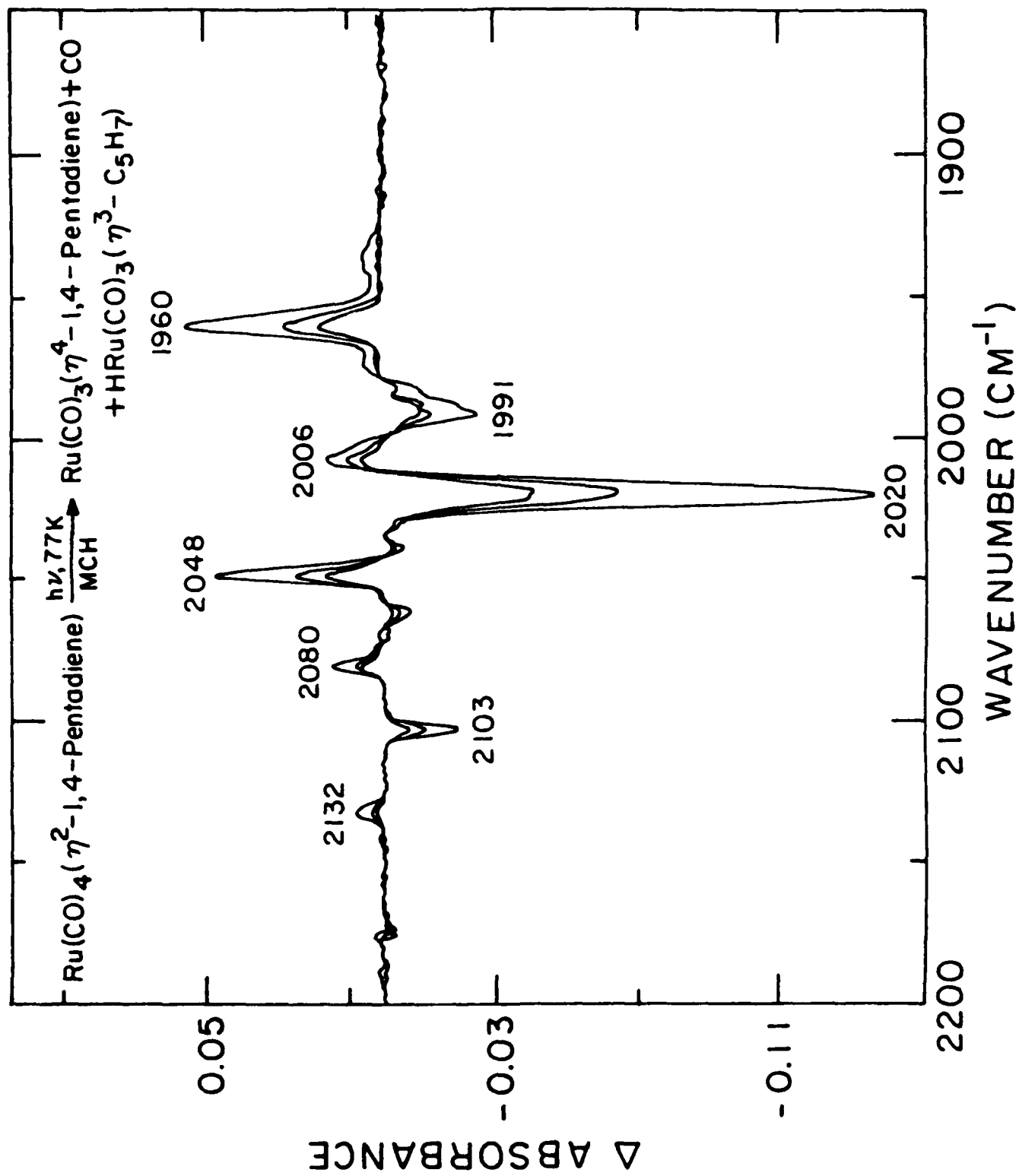
Figure 7. IR difference spectral changes accompanying thermal reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 1,6-heptadiene in 3-methylpentane solution at 298 K ($\Delta t = 30, 60, 90, 120$ s). The positive peaks at 2074 and 1986 cm^{-1} correspond to

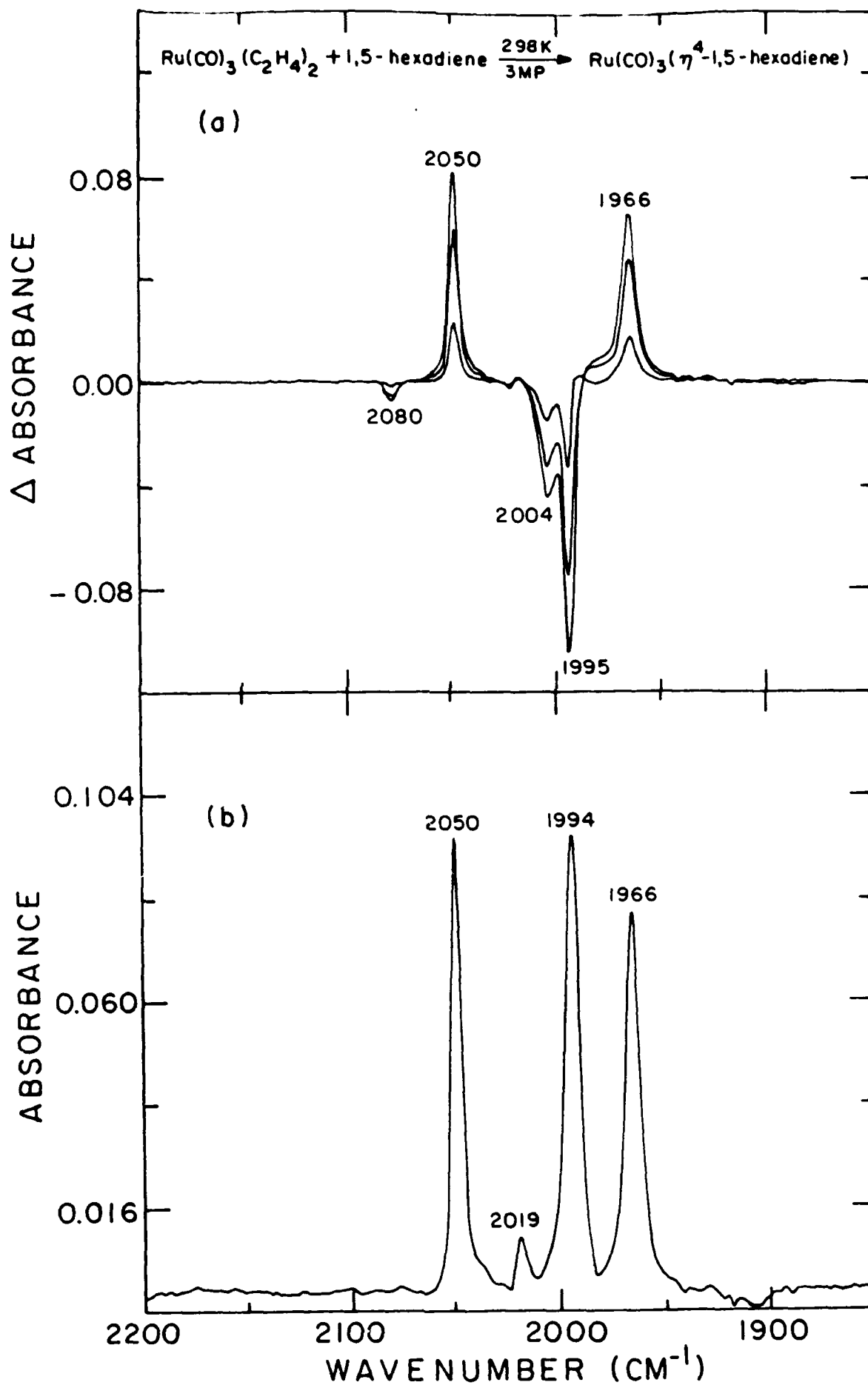


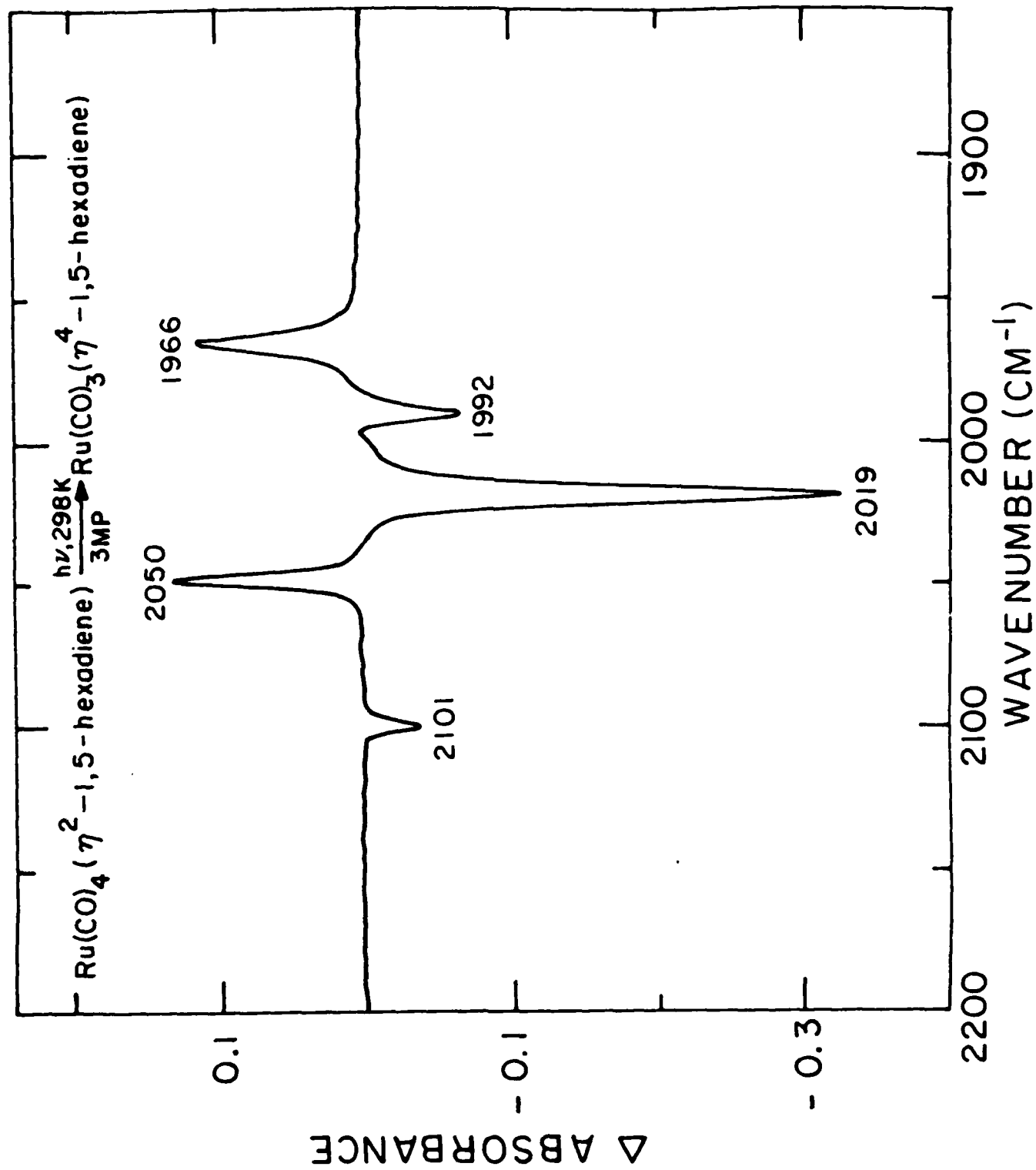


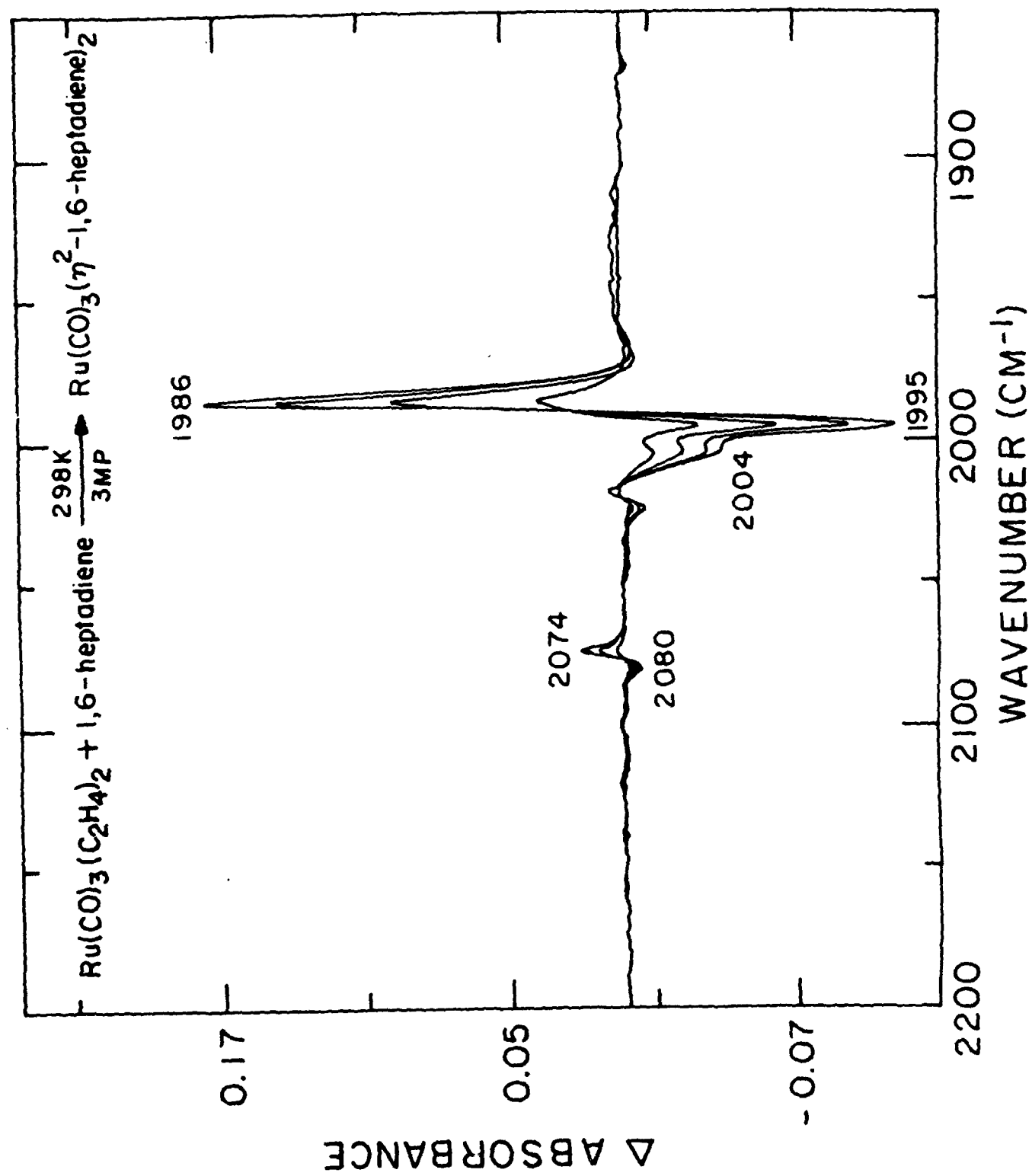












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